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$Sm_{0.5}Sr_{0.5}CoO_3/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ 阴极体系的制备、优化与氧还原动力学研究

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Preparation, optimization and oxygen reduction mechanism of $Sm_{0.5}Sr_{0.5}CoO_3/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$

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目 录

摘要

$Sm_{0.5}Sr_{0.5}CoO_3$(SSC)锶掺杂的钴酸钐是最近报道的一种应用于中温固体氧化物燃料电池(ITSOFC)的高性能阴极材料，负载于镓酸镧电解质上的 SSC 电极性能的优化以及电极上进行的氧还原反应机制的揭示是目前 ITSOFC 研究的重要课题。本文使用 SEM、XRD、EDAX 等分析技术及交流阻抗、极化等电化学研究手段，对负载于掺杂的镓酸镧电解质上的 SSC 阴极进行了系统研究，优化了电极组成及电极体系结构，同时对 SSC 电极上的氧还原反应机理进行了系统分析。

利用在 SSC 电极中掺入 $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$(LSGMC5)电解质粉末的方法，改善了 SSC 阴极在 LSGMC5 电解质片上的烧结性能，提高了电极活性与稳定性。实验发现，LSGMC5 粉末的焙烧温度及其在复合电极中的含量对电极性能的影响显著，当在 SSC 中掺入 15wt%、1473K 焙烧的 LSGMC5 粉末时，复合电极表现出了良好的电化学活性及稳定性。

首次通过在 SSC-LSGMC5(15%wt)阴极与 LSGMC5 电解质之间添加 LSGMC5 电解质材料夹层的方法，改善了电极/电解质界面的微观结构，显著提高了电极性能。结果显示：夹层的加入使得电极/夹层界面取代电极/电解质界面成为反应的关键活性区域，增加了气相/电极/电解质三相界面长度以及电极/电解质两相界面的面积，导致负载在致密夹层上的 SSC-LSGMC5 阴极的氧还原活性远高于没有夹层的样品，在 973K、纯氧条件下，夹层(1673K 焙烧)的引入使电极极化电阻由 0.38 $\Omega \cdot cm^2$ 减小至 0.12 $\Omega \cdot cm^2$，1 A/cm^2 电流密度下的极化过电位由 0.23 V 减小至 0.10 V。该结果揭示了电极/电解质界面对电极性能的显著影响，并提供了一种具有一定创新性的电极优化技术。

建立了 SSC-LSGMC5 复合阴极的氧还原反应模型。SSC-LSGMC 复合电极的氧还原反应包含两个互相竞争的电极反应过程：三相界过程及电极表面反应

过程，此二过程受到反应温度及极化过电位的显著影响。弱极化条件下，氧还原反应主要受三相界过程控制，随着反应温度的降低，其速控步由氧原子扩散过程逐渐转变为电荷转移过程；强极化条件下，电极反应表现为电荷转移步骤控制的电极表面反应过程。添加电解质夹层并未改变电极的反应机理，夹层促进反应的本质原因为增加了反应的活性位。

最后，通过向负载于夹层上的 SSC 复合电极中添加少量的 Pt、Pd 等贵金属有效地进一步提高了电极反应活性。在贵金属负载量小于 0.4 mg/cm^2 的条件下，电极活性随贵金属含量的增加而增加；在 1123K 到 1223K 温度范围内随电极焙烧温度的降低电极性能显著提高。复合电极中的 Pt 在高温下与 LSGMC5 生成不导电的 $SrLaGa_3O_7$ 物相，导致电解质电阻显著增大，而 Pd 的掺入未引起电解质电阻的增加。1123K 焙烧的具有 0.4 mg/cm^2 Pd 负载量的 SSC-LSGMC5 复合阴极具有非常高的电化学反应活性。873K、氧气中、近平衡状态下的电极极化电阻由 0.50 Ω·cm^2 减小至 0.12 Ω·cm^2，0.4 A/cm^2 电流密度下的极化过电位由 0.13 V 减小至 0.065 V。同时，含 Pd 电极交换电流密度的活化能较无 Pd 电极减小约 20 KJ/mol，显示出 Pd 的明显的催化效应。

关键词：固体氧化物燃料电池，$Sm_{0.5}Sr_{0.5}CoO_3$ 阴极，氧还原，夹层，机理

Abstract:

$Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) is one kind of excellent cathode materials for intermediate temperature solid oxide fuel cells (ITSOFC) reported recently. There are growing interests in developing high performance SSC supported on doped $LaGaO_3$ electrolytes, and illustrating the mechanism of oxygen reduction over SSC. Multiple techniques, including SEM, XRD, EDAX, Impedance spectrometry, polarization, were applied to study the SSC electrode supported on $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ (LSGMC5) in this thesis. The composition of the electrode and the structure of the SSC/LSGMC5 assembly were optimized, and the oxygen reduction mechanism over corresponding electrodes was studied systematically.

The addition of LSGMC5 powders into SSC electrode was effective in improving the performance and the stability of SSC electrode supported on LSGMC5. Both the sintering temperature and the amount of LSGMC5 added into SSC have strongly effect on the performance of the electrode. SSC-LSGMC5 composite electrodes consisted of 15 wt % LSGMC5 sintered at 1473K exhibited the highest activity and stability for electrochemical oxygen reduction.

The performance of SSC-LSGMC5 electrode was further improved dramatically by the addition of an LSGMC5 interlayer between an SSC-LSGMC5 electrode and an LSGMC5 electrolyte pellet due to the improved microstructure of the electrode/electrolyte interface. The addition of the interlayer resulted in the shift of the active reaction zone from the electrode/electrolyte interface to the electrode/interlayer interface, which increased the length of the gas/electrode/electrolyte three-phase boundary and the area of the electrode/electrolyte two-phase boundary. The results of electrochemical measurements showed that the polarization resistance of cathode decreased from

0.38 Ω·cm^2 to 0.12 Ω·cm^2, and the over-potential under 1A/cm^2 current density decreased from 0.23V to 0.10V at 973 K in oxygen after the addition of an LSGMC5 interlayer calcined at 1673K. The results demonstrated the strong effect of the structure of the electrode/electrolyte interface on the electrode performance evidently, which could lead to a unique method for electrode optimization.

A model was suggested for illustrating the oxygen reduction over SSC-LSGMC5 composite cathodes. The oxygen reduction reaction over SSC-LSGMC5 composite electrodes could take place through two parallel reaction processes: the three-phase boundary (TPB) process and the surface reaction process. The role of the two processes depended strongly on the reaction temperature and the over-potential applied. Under near equilibrium conditions, the rate-determining step of the reaction changed from the oxygen atom diffusion step to the charge transfer step with the decrease in reaction temperatures, which corresponded to the TPB process and surface reaction process, respectively. Under polarization conditions, the electrode reaction was controlled by the charge transfer step of the surface reaction process. The addition of the interlayer didn't change the reaction mechanism of the electrode, and the improvement in activity by adding an interlayer was due to the extension of the active reaction sites.

The performance of the SSC-LSGMC5 composite cathodes was further improved by the addition of small amounts of Pt or Pd noble metals. The electrode performance increased dramatically with the increase in the amount of the noble metal added and the decrease in the sintering temperature of the electrode within the sintering temperature range of 1123-1223 K, under the condition that the amount of the noble metal introduced was lower than 0.4mg/cm^2. The Pt in SSC-LSGMC5 electrode reacted with LSGMC5 electrolyte at high sintering temperatures, which resulted in the increase in the electrolyte resistance due to the formation of

$SrLaGa_3O_7$. The addition of Pd had no effect on the electrolyte resistance. SSC-LSGMC5 containing 0.4mg/cm^2 Pd exhibited the highest electrochemical performance in our study. The results of electrochemical measurements showed that the polarization resistance of cathode decreased from 0.50 Ω·cm^2 to 0.12 Ω·cm^2, and the over-potential under 0.4A·cm^{-2} current density decreased from 0.13V to 0.065V at 873 K in oxygen after the addition of 0.4mg/cm^2 Pd into the SSC-LSGMC5 electrode. In addition, the activation energy of exchange current density of the electrode containing 0.4mg/cm^2 Pd was 20KJ/mol lower than that of the cathode without Pd, showing an obvious catalytic effect of Pd.

Keywords: Solid oxide fuel cells, $Sm_{0.5}Sr_{0.5}CoO_3$ cathode, Oxygen reduction, Interlayer, Mechanism

第一章 前言

1.1 SOFC的特点

燃料电池是将化学能直接转化为电能的电化学能量转化装置。从原理上讲，燃料电池不受卡诺循环限制，与传统热机相比具有能量转化效率高(可达50%~60%)和环境友好(即很低的NO_x、SO_2和噪音排放)等优点[1]。

早在内燃机问世之前(1842年)，英国的William Grove就展示了世界上第一台以稀硫酸为电解质，H_2为燃料，O_2为氧化剂的电化学能量转化装置[2]。而到本世纪50年代之前，由于电池材料的限制、电极过程动力学理论的落后以及在19世纪后期内燃机这种相对简单的能量转化装置的问世和迅速发展，燃料电池的发展一直处于停滞状态[1]。本世纪中叶，在宇航工业发展的推动下，常温氢氧燃料电池技术有了长足的发展。但当时该类燃料电池系统造价昂贵，只能在航天、军事等特殊场合应用。近年来，由于矿物资源的日趋贫乏和保护生态环境日益受到重视，人们迫切希望发展高效的既可节省有限矿物资源、又可减少污染物排放的环境友好发电技术。燃料电池发电技术正好满足以上要求，重新受到人们的重视。根据燃料电池使用的电解质的不同，目前研究的燃料电池大体可以分为：碱性燃料电池(AFC)、磷酸电池(PAFC)、熔融碳酸盐电池(MCFC)、固体氧化物电池(SOFC)、质子交换膜燃料电池(PEMFC)、直接甲醇燃料电池(DMFC)，各类燃料电池的具体特征见表1-1。其中PEMFC、DMFC本质上均以质子交换膜为电解质，然而两种电池由于燃料的区别对电解质、电极的具体要求显著不同，因此经常作为两类燃料电池进行研究。

SOFC是当前研究非常广泛的一种燃料电池[2-6]。SOFC采用固体氧化物氧离子(O^{2-})导体(如最常用的Y_2O_3稳定的氧化锆，简称YSZ)作电解质起传递O^{2-}和分离空气、燃料的双重作用。这类氧化物由于掺杂了低价金属离子，为了保持整体的电中性，晶格内产生大量的氧空位，在高温下(600-1000℃)，氧空位的迁移